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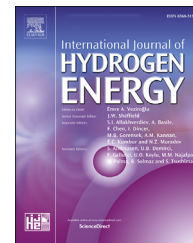
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# Beyond Haber-Bosch: The renaissance of the Claude process

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## HIGHLIGHTS

- Ammonia may be one of the hydrogen carriers of the future.
- The technical and economical feasibility of a single-pass ammonia synthesis process is discussed.
- A single-pass ammonia synthesis process is cost competitive with the Haber-Bosch synthesis loop at small scale.

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## ABSTRACT

Ammonia may be one of the energy carriers in the hydrogen economy. Although research has mostly focused on electrochemical ammonia synthesis, this however remains a scientific challenge. In the current article, we discuss the feasibility of single-pass thermochemical ammonia synthesis as an alternative to the high-temperature, high-pressure Haber-Bosch synthesis loop. We provide an overview of recently developed low temperature ammonia synthesis catalysts, as well as an overview of solid ammonia sorbents. We show that the low temperature, low pressure single-pass ammonia synthesis process can produce ammonia at a lower cost than the Haber-Bosch synthesis loop for small-scale ammonia synthesis ( $<40 \text{ t-NH}_3 \text{ d}^{-1}$ ).

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## Introduction

'It may be that this solution is not the final one,' Fritz Haber proclaimed during his 1918 Nobel Laureate acceptance speech for the development of thermo-catalytic ammonia synthesis from hydrogen and nitrogen (Equation (1)). Many have heeded this as a call for the development of an electrochemical ammonia synthesis process over the past few decades [1–9].

However, electrochemical ammonia synthesis remains an unsolved research problem [10–13].

Incremental improvements to the conventional, Haber-Bosch ammonia synthesis loop and coupling this process with green hydrogen production technologies (and nitrogen purification technologies) have proved most feasible so far [14]. Smith et al. [15] discussed alternatives for a green Haber-Bosch processes, as well as the potential for a single

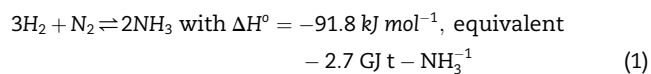
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pass ammonia synthesis process. Ammonia may play a role as an energy vector in the decarbonized energy landscape [15–20].



In the current work we aim to show how a single pass, absorbent-enhanced ammonia synthesis process is cost competitive with a high-pressure Haber-Bosch synthesis loop for decentralized applications, due to low capital expenditure required for the single pass, absorbent-enhanced process [15]. Small-scale power-to-ammonia plants may find applications for isolated communities in for instance the interior of Africa, as ammonia may be an energy storage medium that accounts for the intermittency of renewables such as wind and solar [18,21]. We aim to shed light on how such a single-pass, absorbent-enhanced process is conceivable in the near future with materials reported in literature, allowing for operation at or even below 200 °C. This potentially allows for operating the ammonia synthesis reaction and ammonia separation at nearly the same temperature, thereby minimizing the cost for heat exchange within the ammonia synthesis section. Furthermore, ammonia synthesis and ammonia separation can be operated in the same vessel, thereby reducing the investment cost for the ammonia synthesis section [15].

### Learning from history: the Claude process

The single pass conversion in the Haber-Bosch process is typically 10–15% [22,23]. Ammonia synthesis occurs over a catalyst bed with multiple-promoted iron catalysts at 400–500 °C and 100–300 bar. The ammonia is separated via condensation at near-ambient temperatures. Due to the low single-pass conversion of 10–15% under the Haber-Bosch conditions (400–500 °C and 100–300 bar), a recycle is required for effective utilization of the feed gas, typically leading to overall conversions of 97–99% [15]. However, it is desirable to have a near-complete single-pass conversion, as this would allow for smaller equipment sizes and would alleviate the requirement of an expensive recycle compressor. The single pass conversion can be increased by (1) increasing the equilibrium conversion in the reactor, and by (2) separating the ammonia more completely than by condensation, decreasing the ammonia concentration entering the reactor again after the separation step. The separation by condensation at a given temperature is limited by the vapour pressure of ammonia at that temperature. For reference, the vapour pressure of ammonia is about 8.5 bar at room temperature.

The first attempt at a single pass ammonia synthesis process was demonstrated by the French engineer Georges Claude in 1917 [24]. As opposed to operating at the 200 bar of the first Haber-Bosch plants [25], Claude proposed to increase operating pressure to 900–1000 bar. Due to the logarithmic scaling relation between the pressure increase and the work required, the energy requirement for compression from 1 bar to 900–1000 bar is only 1.2 times the energy required for

compression to 200 bar [26]. Multi-stage compression is required to increase the pressure from 1 bar to 900–1000 bar.

At such *hyperpressures*, the equilibrium conversion is increased such that single pass conversions of 40% per reactor can be attained at 500–650 °C [27,28]. The ammonia is subsequently condensed, after which the mixture of nitrogen and hydrogen is fed to a second ammonia synthesis reactor. The overall conversion can be above 80% after a cascade of three to four reaction and condensation steps, eliminating the requirement for a recycle (see Fig. 1). The residual gas is used for heating purposes for hydrogen production. In industrial practice, the Claude process did not live up to its promises due to technical problems caused by the severe operating conditions [24]. For example, the use of hyper-pressures also results in high partial pressures of catalyst poisons such as O<sub>2</sub> and H<sub>2</sub>O, thereby decreasing the catalyst activity. Furthermore, pipe corrosion, hydrogen-embrittlement and pipe bursts are more likely to occur at higher pressures, implying more expensive piping material is required. At the end, the Claude process could not compete with the Haber-Bosch process.

### The single pass ammonia synthesis process of the 21st century

Even though the Claude process has demonstrated that a single pass ammonia process is conceivable, other strategies should be employed for increasing the single pass conversion of ammonia under mild conditions. With the recent trend of coupling intermittent renewables such as solar, tidal and wind resources to electrolyzers, there is desire for operation under mild operating conditions, rather than at *hyperpressures*, as this allows for better intermittent operation. Examples of such developments are increased catalyst activity at low temperature (<300 °C) [29–31], as well as the use of solid sorbents for more complete ammonia removal [32–35]. Operation at low temperature improves the equilibrium to ammonia, which allows for operation under milder pressures.

In the upcoming sections, we discuss the technological feasibility of a single-pass system, based on literature. We set targets for the desirable ammonia synthesis catalyst and ammonia sorbent. Preferably, the ammonia synthesis reactor and the ammonia separation operate at the same temperature [36], as this alleviates the need for expensive equipment for heat integration [15]. Ideally, the heat of reaction, i.e. 2.7 GJ t-NH<sub>3</sub><sup>-1</sup> (Equation (1)), suffices for the desorption of ammonia from the sorbent. If the reaction operates at a similar temperature as the absorption, desorption would require a higher temperature. Therefore, heat integration by using the heat of reaction to drive the desorption is not feasible and additional energy is always required. If the NH<sub>3</sub> is stored in the sorbent, the heat of reaction cannot be used to drive desorption in any case.

In section Solid sorbents for ammonia separation, ammonia sorbents are discussed, to identify the most suitable sorbents for ammonia separation. Subsequently, recent achievements in catalyst development are discussed in section Catalysts. After this, a cost breakdown is provided for a small-scale single-pass ammonia synthesis process, as compared to benchmark electrolysis-based Haber-Bosch

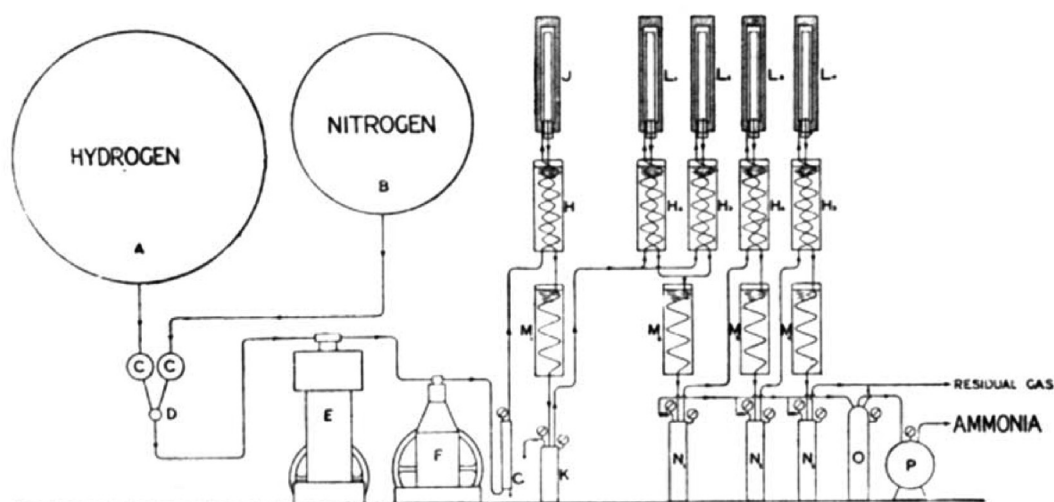


Fig. 1 – Schematic representation of the Claude process. Reproduced from Ref. [28].

processes, and absorbent-enhanced Haber-Bosch processes. These processes are elaborated upon in section The single pass process in perspective. A conventional fossil-based Haber-Bosch process is not considered here, as this process cannot be scaled down cost effectively due to the extensive heat exchange required between the steam methane reforming (SMR) section and the ammonia synthesis loop [15].

#### Solid sorbents for ammonia separation

Academic research mostly focused on improving the activity of ammonia synthesis catalysts to lower the ammonia synthesis temperature and pressure [37]. However, selective and complete removal of ammonia from the reactor effluent is another prerequisite for ammonia synthesis under mild conditions. Complete removal of ammonia via condensation from the gas stream is difficult and operation at low pressures (<50 bar) is not feasible, due to the significant ammonia vapour pressure at ambient conditions (8.5 bar at 20 °C) [15,18].

Ammonia can be removed more completely by solid sorbents, depending on the sorbent capacity and affinity to bind ammonia, and sorption kinetics [34,38]. Interestingly, Georges Claude already patented the capture of ammonia in the solid form of ammonium chloride as early as 1924 [39]. Over the past two decades, various research groups have worked on ammonia separation at Haber-Bosch conditions with solid sorbents [33,34,40–46].

A wide range of materials has been proposed for ammonia separation, such as activated carbon [47,48], covalent organic frameworks [49], deep eutectic solvents [50], ionic liquids [51], metal organic frameworks [52], metal halides [42], oxides [53], porous organic polymers [54], and zeolites [47,48]. Among these, metal halides and zeolites are most feasible, as these are already applied in other industrial processes and the technology readiness level (TRL) is higher than that of other materials. Ammonia is adsorbed on zeolites, while ammonia is absorbed in metal halides, forming a solid solution. The ammonia absorption/adsorption and desorption mechanisms in metal halides and zeolites are reviewed in Refs. [55–57].

Ammonia separation technologies by condensation, metal halides and zeolites are listed in Table 1.

The concept to be evaluated is a single vessel, in which the ammonia synthesis reaction and separation occurs. The ammonia synthesis reaction and the ammonia separation occur in different beds within the same vessel. Important descriptors to evaluate sorbents are (1) the sorbent capacity, (2) the heat of desorption and the heat required for heating the sorbent, (3) the operating temperature window, and (4) the equilibrium ammonia pressure window [60]. The sorbent capacity determines the size of the separator bed and therefore the capital investment required. Optimization of the sorbent material and morphology can increase the rate of absorption/adsorption and desorption, as well as the total sorbent capacity [42,61,62]. As listed in Table 1, similar ammonia capacities are attainable for metal halides and zeolites.

The heat of desorption determines the energy required for obtaining purified ammonia. For zeolites, typical values for the heat of adsorption are  $-155 \text{ kJ mol}^{-1}$  to  $-100 \text{ kJ mol}^{-1}$  (about  $6\text{--}9 \text{ GJ t-NH}_3^{-1}$ ) [59]. As shown Table S1 and in Figure S1, the heats of absorption for subsequent absorption steps on metal halides is substantially lower with typical values of  $40\text{--}90 \text{ kJ mol}^{-1}$  (about  $2.4\text{--}5.3 \text{ GJ t-NH}_3^{-1}$ ) [63,64]. Furthermore, the temperature window of absorption/adsorption and desorption determines the heat integration required between the ammonia synthesis reactor and the ammonia separation within the vessel. Heat exchangers are major cost contributors to conventional ammonia synthesis loops with about 45% of the capital expenditure [15].

Ammonia adsorption on zeolites requires low temperatures of  $20\text{--}100 \text{ °C}$  for a reasonable ammonia capacity [48], which implies the cost of heat exchangers is similar to separation with condensation. Thus, low pressure ammonia separation with zeolites is not expected to provide a substantial cost benefit over high-pressure separation by condensation. On the other hand, ammonia absorption in metal halides can be operated in a wider temperature window and closer to the reaction temperature [35]. This allows for a substantial decrease in the heat exchanger surface area and might even

**Table 1 – Comparison of ammonia separation technologies. The energy consumption includes the energy required for cooling or heating, as well as the energy required for compression and liquefaction. Based on [18,42,58,59].**

	Condensation	Metal halides	Zeolites
Separation temperature (°C)	–20 to 30	150–250 <sup>d</sup>	20–100
Desorption temperature (°C)	–	300–400 <sup>d</sup>	200–250
Pressure (bar)	100–1000	10–30	10–30
Heat of adsorption (kJ mol <sup>–1</sup> )	–	–90 to –40	–155 to –100
Energy consumption (GJ t <sub>NH<sub>3</sub></sub> <sup>–1</sup> )	3–5 <sup>c</sup>	6–11 <sup>e</sup>	8–13 <sup>e</sup>
NH <sub>3</sub> concentration in gas phase after separation step (mol.%)	2–5	0.1–0.3	0.1–0.3
Ammonia storage capacity (wt.%) <sup>a</sup>	100	5–30	5–15
Ammonia density (kg m <sup>–3</sup> ) <sup>b</sup>	680	100–600	30–90
Examples	–	CaCl <sub>2</sub> , MgCl <sub>2</sub> on oxides	Mol. sieve 4A, 5A, 13 X
TRL	9	4–5	4–5

<sup>a</sup> This is defined as the weight fraction of ammonia as part of the weight of the fully loaded adsorbent (tank material excluded).

<sup>b</sup> This is defined as the ammonia density per volume storage vessel.

<sup>c</sup> The energy consumption increases to 20–25 GJ t<sub>NH<sub>3</sub></sub><sup>–1</sup> at 20 bar [15].

<sup>d</sup> These are typical values used in literature. However, the separation temperature and desorption temperature vary widely with the metal halide and the amount of ammonia absorbed.

<sup>e</sup> The estimated energy consumption is determined by both the heat of desorption and the energy required for heating the sorbent.

open the possibility for separation of the ammonia during reaction [36]. Thus, metal halides are the most suitable alternative for a potential low pressure, single-pass ammonia synthesis process. It should be noted that heating the sorbent also amounts to 3–4 GJ t<sub>NH<sub>3</sub></sub><sup>–1</sup> per 100 °C heating [65].

The fundamentals of the ammonia absorption-desorption mechanism in metal halides are well studied [61], and current research efforts should focus on engineering challenges for stable operation during months to years. The use of pure metal halides is not feasible, as the particles are not stable under desorption conditions (300–400 °C) due to particle agglomeration [34]. Thus, the development of commercial metal halide-based ammonia sorbents with long-term stability requires additional research [42,66]. A pathway to enhance the sorbent stability is the use of inert supports such as oxides or carbon supports for metal halide sorbents such as CaCl<sub>2</sub> and MgCl<sub>2</sub>, among others [42,66]. A drawback of this is that the maximum theoretical sorbent capacity decreases. However, the reported capacities of supported metal halides is higher than for unsupported particles, due to the higher attained external surface area [42].

## Catalysts

In the current section, we discuss historical developments, as well as the state-of-the-art for ammonia synthesis catalysts in order to answer the question: to what extent can ammonia be synthesized at temperatures desired for separation (e.g., about 150 °C, see Figure S1 in the supplementary information)?

In industry, multiple promoted iron-based catalysts are primarily used, operating at 400–500 °C [67]. Following the development of the multiple promoted iron catalyst by Mitasch and coworkers in the early 1910s [68], the industrial iron catalyst has remained remarkably similar, apart from minor changes in catalyst formulation and optimization of catalyst preparation [23].

Activated carbon supported ruthenium-based catalysts (Ru/AC) have also been implemented industrially [23]. Even

though some energy efficiency gains were achieved with Ru/AC as compared to iron-based catalysts due to a higher activity, the implementation of such catalysts has been limited, due to a higher catalyst cost and a shorter catalyst lifetime in presence of methane [67].

For both the industrial iron-based catalysts and first generation of Ru-based catalysts (Ru/AC, Ru/Oxide), N<sub>2</sub> dissociation is the rate limiting step, which can be enhanced by the introduction of alkali and alkaline earth promoters [69], lowering the barrier for N<sub>2</sub> dissociation [70].

In recent years, the groups of Hara and Hosono have changed the paradigm that N<sub>2</sub> dissociation is the rate-determining step for ammonia synthesis [72]. Over the past decade, Ru-based catalysts on new support materials, i.e. electrides (C<sub>12</sub>A<sub>7</sub>:e<sup>–</sup>), ammines (Ca–Ba(NH<sub>2</sub>)<sub>2</sub>), and fluorides (CaFH) (see Fig. 2) with substantially enhanced activity have been developed [29–31,71–78]. The improvement has been explained based on the electronic properties of the new support materials. The electride C<sub>12</sub>A<sub>7</sub>:e<sup>–</sup> consists of a positively charged framework with the chemical formula [Ca<sub>24</sub>Al<sub>28</sub>O<sub>64</sub>]<sup>4+</sup> and 4 extra-framework electrons, accommodated in the cages as counter ions [79] and is stable at ambient temperature. For this second generation Ru-based catalysts, hydrogenation over the catalyst is the rate-limiting step, rather than the N<sub>2</sub> dissociation step [72]. These substantially more active Ru-based catalysts show ammonia synthesis activities at 200–250 °C similar to activities of industrial Fe-based catalysts and the first generation Ru-based catalysts (Ru/AC, Ru/Oxide) at 350–400 °C (see Fig. 3) [29,30]. Thus, the second-generation Ru-based catalysts is active at lower temperatures enabling higher equilibrium ammonia concentrations (see Fig. 3 and Figure S7), resulting in similar activity like the commercial catalysts, achieving the same productivity per unit of reactor volume but at lower temperatures. The long-term thermal stability as well as resistance against poisons such as H<sub>2</sub>O and O<sub>2</sub> of the second-generation Ru-based catalysts needs to be understood for practical operation. So far, a stable activity for a few days has been reported [30]. For reference, commercial



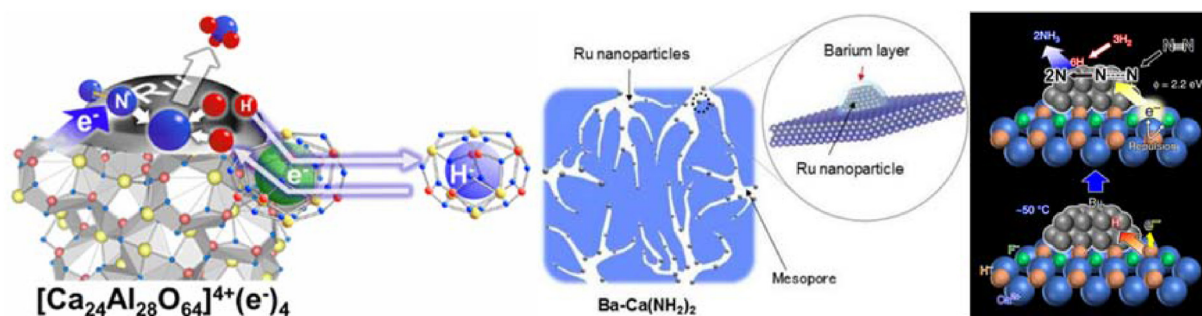


Fig. 2 – Examples of 2nd generation Ru-catalysts with substantially enhanced electronic support properties. Left: Ru/ $\text{C}_{12}\text{A}_7:\text{e}^-$ . Middle: Ru/Ba–Ca(NH<sub>2</sub>)<sub>2</sub>. Right: Ru/CaFH. Reproduced from Refs. [29,30,71].

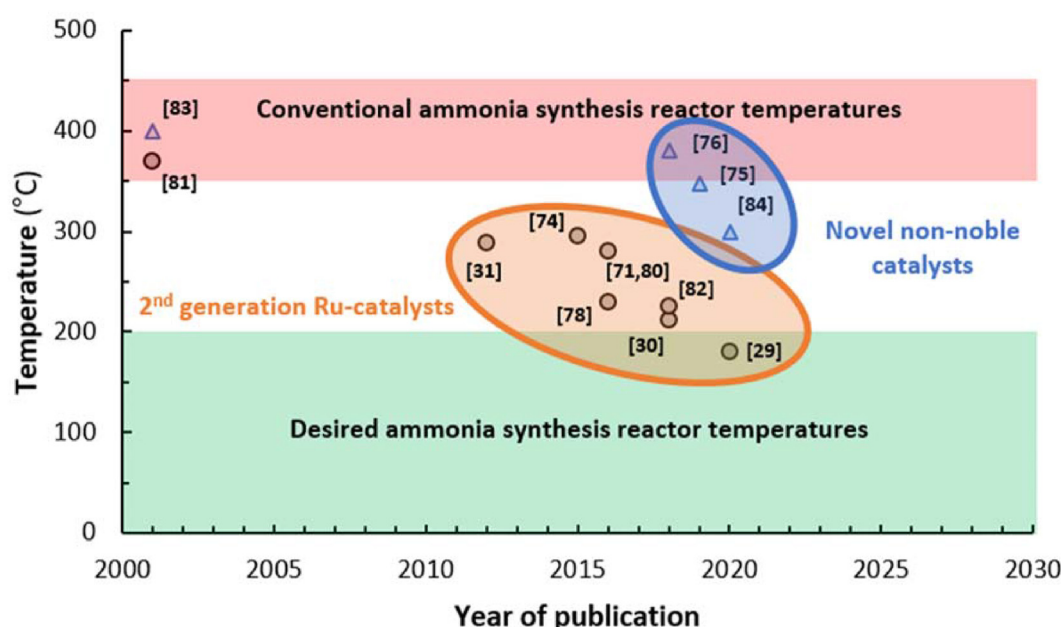


Fig. 3 – Reaction temperatures required for ammonia synthesis rates of 1 mmol g<sup>-1</sup> h<sup>-1</sup> at 1 bar, H<sub>2</sub>:N<sub>2</sub> = 3:1 and 60 mL min<sup>-1</sup>, catalyst loading 0.1 g. It should be noted that the operational pressure in a single pass process is typically higher than 1 bar, as the outlet pressures for hydrogen production and nitrogen production typically have outlet pressures of at least 10 bar (see supporting information). Inspired by Ref. [5]. Original references Ru [29–31,71,74,78,80–82], and Co & Ni [75,76,83,84].

Fe-based and Ru-based catalysts have a lifetime of more than 10 years [23].

The reported cost of Fe-based catalysts is 1.8 € kg-catalyst<sup>-1</sup>, while the reported cost of Ru/AC is 270–415 € kg-catalyst<sup>-1</sup> [67,85]. According to Yoshida et al. [85], Ru-based catalyst can account to a significant portion of the operational cost for ammonia production. However, the higher activity of Ru-based catalysts results in a lower energy consumption, and smaller reactor sizes. Thus, the cost for ammonia loop with a Fe-based catalyst and a Ru-based catalyst is similar for the current Ru price of about 1000 € kg-Ru<sup>-1</sup> [85]. It should be noted, however, that the authors did not consider Ru recovery from utilized Ru-based catalysts, which is typically over 90% of the catalyst material [86].

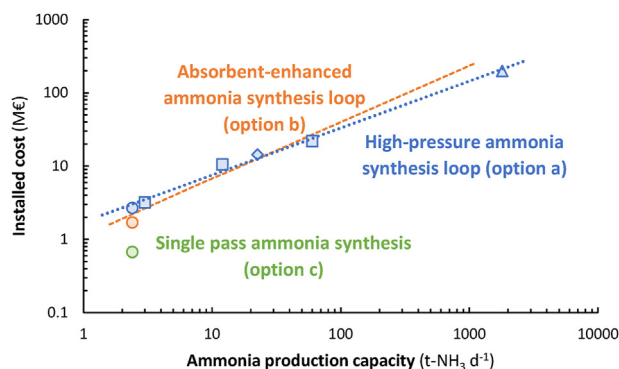
Non-noble catalysts with low-temperature activity for ammonia synthesis are also developed, thereby decreasing the cost and scarcity of the catalyst materials. In recent years, various Co-based and Ni-based NH<sub>3</sub> synthesis catalysts with low temperature activity have been reported [87,88]. The current cost of Co and Ni is about 35–40 € kg-Co<sup>-1</sup> and 15 € kg-Ni<sup>-1</sup>, respectively, i.e. far below the cost of Ru. As shown in Fig. 3, novel non-noble Co-based and Ni-based catalysts with significant activity below 400 °C have been developed [87,89]. However, non-noble catalysts with a high ammonia synthesis activity below 200 °C have not yet been reported. Time will tell whether the rapid developments for Ru-based catalysts in recent years can be translated to non-noble catalysts.

## Process proposal & economics

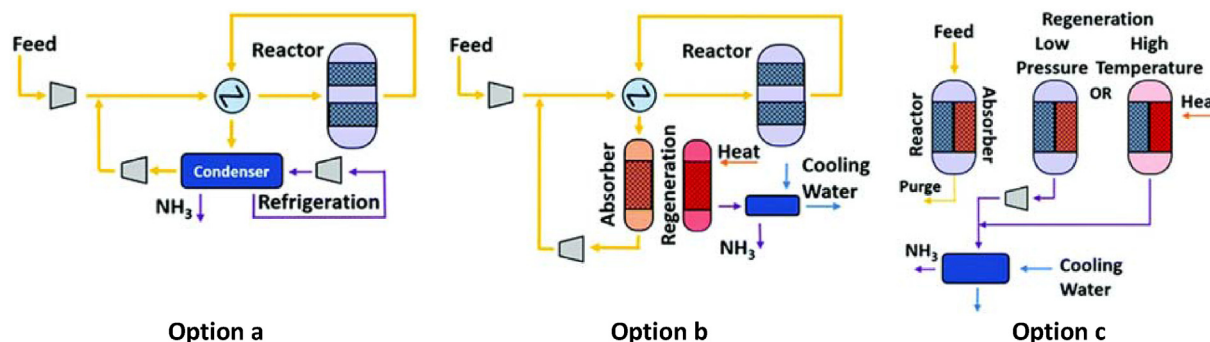
As discussed in the previous sections, ammonia synthesis at low temperatures (at or below 200 °C) has recently become possible with Ru-based catalysts, but not with non-noble catalysts. Next, we discuss the potential single pass ammonia synthesis processes of the 21st century.

The electrolysis-based, conventional high-pressure Haber-Bosch process with condensation (option a), the electrolysis-based absorbent-enhanced Haber-Bosch process (option b), and the absorbent-enhanced single-pass ammonia synthesis process (option c) are compared. The process diagrams for the process alternatives are shown in Fig. 4.

Alternatives for hydrogen production by electrolysis and alternatives for nitrogen production are discussed in the [supplementary information section S2](#). For all ammonia production processes considered, hydrogen is produced with a polymer electrolyte membrane (PEM) electrolyzer at 15 bar. An advantage of PEM electrolysis is the flexibility, allowing for rapid load changes caused by use of wind and solar [90]. A small H<sub>2</sub> tank is needed to buffer power fluctuations, which has a minor effect on the total cost of ammonia production (10 € t-NH<sub>3</sub><sup>-1</sup>) [91]. It should be noted that this results in essentially no CO<sub>2</sub> footprint for all NH<sub>3</sub> synthesis options, as the H<sub>2</sub> produced with an electrolyzer is derived from renewable electricity. Nitrogen is produced by pressure swing adsorption (PSA), which is the most feasible alternative at the process scale proposed (3 t-NH<sub>3</sub> d<sup>-1</sup>) [18,92]. As hydrogen and nitrogen are already produced at elevated pressures, little to no compression is required for the ammonia synthesis loop in case of sorbent-enhanced ammonia synthesis loops. Ammonia can be synthesized at 200–250 °C with second-generation Ru-based catalysts, which is especially required for option c (the single-pass ammonia synthesis process) due to the high equilibrium ammonia concentration at low temperatures. These highly active catalysts can also be used for option a (the high-pressure Haber-Bosch process) and option b (the absorbent-enhanced Haber-Bosch process) in order to decrease the requirement for heat integration between the



**Fig. 5** – Installed cost for the ammonia synthesis loop, for the conventional high-pressure ammonia synthesis loop (option a, marked in blue), absorbent-enhanced ammonia synthesis loop (option b, marked in orange), and single pass ammonia synthesis loop (option c, marked in green). The cost of a high-pressure ammonia synthesis loop with a capacity of 1800 t-NH<sub>3</sub> d<sup>-1</sup> (blue triangle) was reported by Appl [93]. The cost of the 3, 12, and 60 t-NH<sub>3</sub> d<sup>-1</sup> high-pressure ammonia synthesis loops (blue squares) are based on quotes provided by Proton Ventures, partially reported in Banares-Alcantara et al. [94], in Rouwenhorst et al. [56], and in Vrijenhoef [95]. The cost of a 22.5 t-NH<sub>3</sub> d<sup>-1</sup> high-pressure synthesis loop (blue diamond) was previously reported in Rouwenhorst et al. [56]. The cost breakdown of the installed cost for various ammonia synthesis loops (option a, b, and c) with a capacity of 2.4 t-NH<sub>3</sub> d<sup>-1</sup> (blue, orange, and green circles) are reproduced from Smith et al. [15]. A cost breakdown of the data from Smith et al. [15] can be found in [Figure S12](#). The orange line represents a cost-scaling relationship for an absorbent-enhanced Haber-Bosch synthesis loop, as proposed by Palys et al. [96]. The blue line represents a cost-scaling relationship for a high-pressure Haber-Bosch synthesis loop, based on the data points in the Figure (order is 0.64, R<sup>2</sup> = 0.99). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 4** – Process diagrams for the conventional high-pressure Haber-Bosch process with condensation (option a), the absorbent-enhanced Haber-Bosch process (option b), and the single-pass ammonia synthesis process (option c). In case of option c, ammonia synthesis and ammonia absorption occurs in the same vessel, but in different beds. Schematic diagrams reproduced from Ref. [15].

synthesis reactor and the ammonia separation, as elaborated in [supplementary information section S2.1-S2.2](#).

The capital investment for the various process technologies, as well as energy requirement for ammonia synthesis are discussed hereafter. As shown in [Fig. 5](#), the investment cost for a high-pressure ammonia synthesis loop (option a) is significantly higher than the installed cost for absorbent-enhanced processes (option b and c) at low ammonia production capacities of below  $10 \text{ t-NH}_3 \text{ d}^{-1}$ . The high-pressure Haber-Bosch synthesis loop benefits from large scale application, with a cost scaling factor of 0.64. A dominant cost factor is the feed compressor, which amounts to over 50% of the CapEx in the ammonia synthesis loop at capacities below  $10 \text{ t-NH}_3 \text{ d}^{-1}$  (see [Figure S12](#)) [15,85]. Thus, absorbent-enhanced ammonia synthesis loops operating at the same pressure as  $\text{H}_2$  and  $\text{N}_2$  production benefit from small scale-operation.

For option b and option c, ammonia can be separated at  $150\text{--}200^\circ\text{C}$  with for instance  $\text{MgCl}_2/\text{SiO}_2$ . In case of option c, ammonia synthesis and ammonia separation are integrated in the same vessel with a heat exchanger in between the beds, or by mixing the catalyst and absorbent, thereby reducing the investment cost for the ammonia synthesis section [15]. If not feasible, the steps can also be operated in separate vessels. An overall conversion of 100% is assumed for the  $\text{H}_2$  and  $\text{N}_2$  in case of option a and option b. On the other hand, the overall conversion is assumed to be about 89% for option c, with a total energy consumption of  $41 \text{ GJ t-NH}_3^{-1}$ , which is due to not recycling the residual  $\text{H}_2$  and  $\text{N}_2$  after the third reaction-separation step (see [supplementary information S2.3](#) for additional discussion). For reference, the total energy consumption of option a is  $35 \text{ GJ t-NH}_3^{-1}$ , while option b consumes  $38 \text{ GJ t-NH}_3^{-1}$  (see [Fig. 6](#) and [supplementary information S2.2](#)). These values for the energy consumption are in line with values reported in literature [18,91,97,98]. The process conditions, the materials used, and the energy required per process step can be found in the [supplementary information section S2.2](#), while a discussion and calculations regarding the number of reaction-separation steps for the single pass ammonia

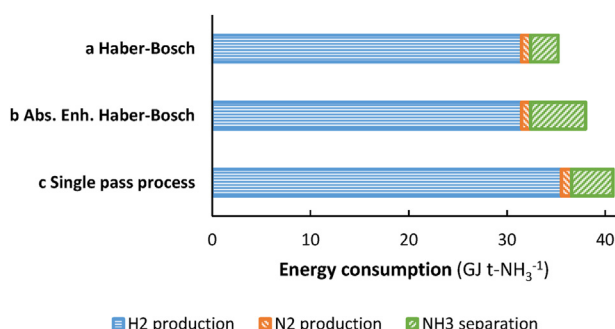
process can be found in the [supplementary information section S2.3](#).

[Fig. 7](#) compares investment costs for option a, option b, and option c, as discussed in detail in [supplementary information section S2.4](#), with a cost breakdown for the capital investment and operational expenditure. Clearly, ammonia can be synthesized at the lowest capital cost in case of option c. For option c, the  $\text{N}_2$  and  $\text{H}_2$  feeds flow only once through the heat exchangers, minimizing the heat exchanger area required, and no recycle compressor is needed. For an ammonia synthesis rate of  $3 \text{ t-NH}_3 \text{ d}^{-1}$  (equivalent to about 1 MW input power), operational for 350 days per year, and with electricity costs of  $20\text{--}40 \text{ €/MWh}^{-1}$ , the ammonia production cost of the single-pass process (option c) is up to  $60 \text{ €/t-NH}_3^{-1}$  lower than option a and option b due to a lower capital expenditure (see [Fig. 7](#)).

The effect of the number of operational days per year on the cost of ammonia was also assessed for option a and for option c (see [Figure S8](#)). For less operational days per year, the cost of ammonia increases, due to the higher contribution of the capital expenditure. Due to the smaller ammonia synthesis section for option c, the cost penalty for less operational hours is smaller than for option a and option b. At low operational load (150 days per year), the cost difference between the option c and option a is more than  $150 \text{ €/t-NH}_3^{-1}$  (see [Figure S8](#)). Additional discussion can be found in the [supplementary information section S2.4](#).

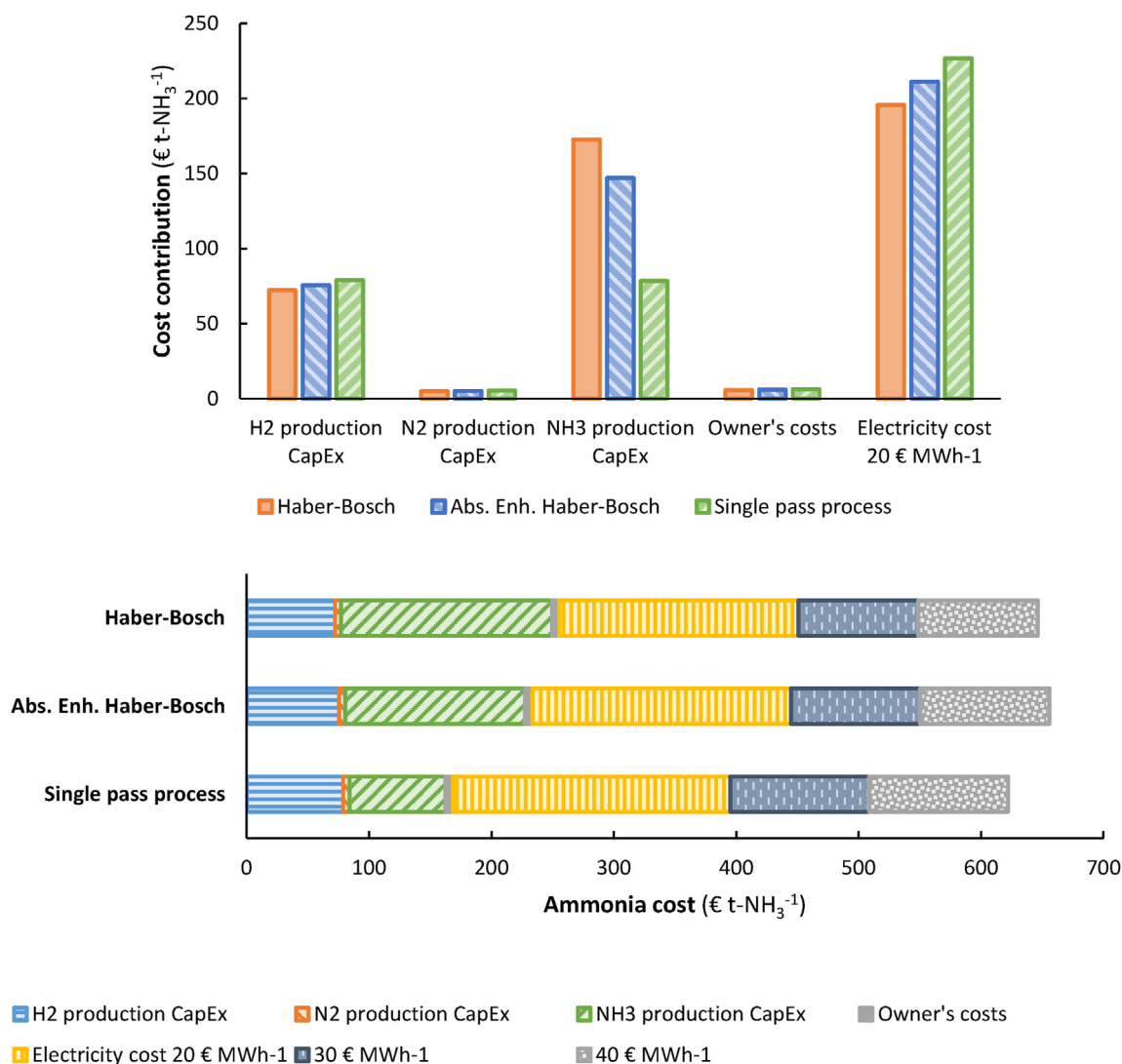
[Fig. 8](#) shows the effect of the ammonia production capacity on the cost of ammonia for option a and for option c. Upon scale-up, the contribution of the capital investment decreases, and the contribution of the energy consumption becomes dominant. The effect of an increased production capacity favours option a, as a result of a lower energy consumption for option a than for option c, as shown in [Fig. 8](#). This is due to the lower overall conversion in case of option c (89%), as compared to option a (100%). Thus, large scale ammonia production with capacities above  $30 \text{ t-NH}_3 \text{ d}^{-1}$  is probably still by the Haber-Bosch process in the decades to come.

Electrolysis for  $\text{H}_2$  production, air separation for  $\text{N}_2$  production, and  $\text{NH}_3$  synthesis with the high-pressure Haber-Bosch process are already industrially applied (TRL = 8–9), so the cost of these technologies is known from industrial quotes and no uncertainty analysis was performed for these steps. To account for the uncertainty of the cost estimates of the single pass process, a sensitivity analysis can be found in [Figure S10](#) and [Figure S11](#) in the [supplementary information](#), from which it follows that the single pass process is only advantageous at small scale ( $<10 \text{ t-NH}_3 \text{ d}^{-1}$ ) when the maximum energy consumption is  $45 \text{ GJ t-NH}_3^{-1}$  and/or the investment cost for the  $\text{NH}_3$  synthesis loop does not increase by more than 50% compared to the base case cost estimate. From this analysis, it follows that the single pass process is a promising technology, but a proof-of-concept is required to assess the competitiveness with the Haber-Bosch process in terms of energy consumption and capital investment. It should be noted that the analysis does not include the effects of uncertainties imposed by the use of wind or solar energy on optimal design of the technology, as discussed by Verleysen et al. [19].



**Fig. 6 – Net energy consumption for the electrolysis-based conventional Haber-Bosch process (a), the electrolysis-based absorbent-enhanced Haber-Bosch process (b), and the single-pass ammonia synthesis process (c). In case of the single-pass ammonia synthesis process, the overall conversion is 89% (see [supplementary information section S2.3](#)).**





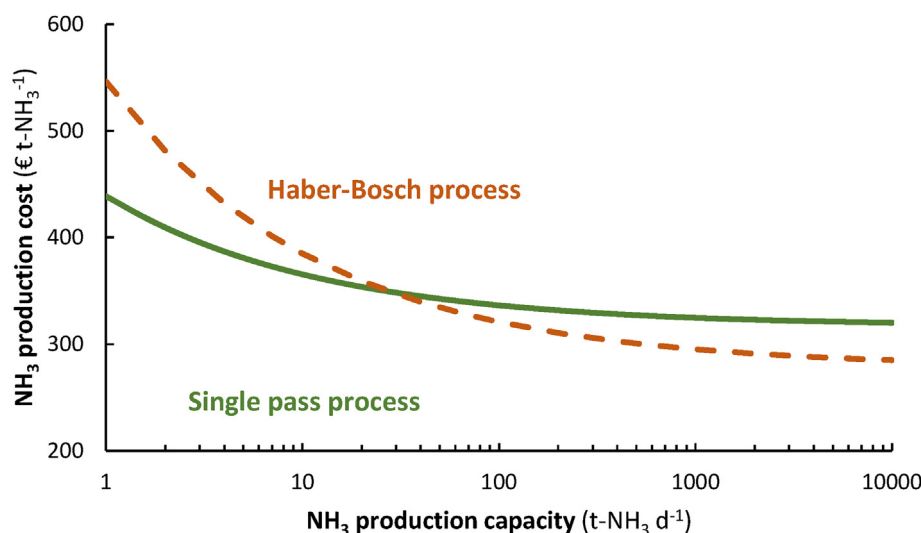
**Fig. 7 – Top:** cost contributions for the investment costs of H<sub>2</sub> production, N<sub>2</sub> production, and NH<sub>3</sub> production, and the operational expenditures such as the electricity cost and the owner's costs, at a capacity of 3 t-NH<sub>3</sub> d<sup>-1</sup> operational for 350 days per year at an electricity cost of 20 € MWh<sup>-1</sup> in 2030. **Bottom:** Cost of ammonia synthesis at a capacity of 3 t-NH<sub>3</sub> d<sup>-1</sup> operational for 350 days per year at an electricity cost of 20, 30, or 40 € MWh<sup>-1</sup> in 2030. See the [supplementary information section S2.2 and S2.4](#) for process conditions, assumptions, and calculations. For the conventional high-pressure Haber-Bosch process, and the absorbent-enhanced Haber-Bosch process, novel catalyst designs are taken into account for estimating the heat exchanger area in order to provide a fair comparison. A breakdown of the investment cost for the ammonia synthesis loop is shown in [Figure S12 in the supplementary information](#).

### The single pass process in perspective

In the current work, we highlight an electrolysis-based low temperature, low pressure single pass ammonia synthesis process for small scale applications. However, various other technologies are also researched as an alternative to the conventional process. In the current section, we briefly address the state-of-the-art of other novel renewable ammonia synthesis technologies.

As discussed in the introduction, electrochemical ammonia synthesis is widely studied [1–9]. A potential benefit of electrochemical ammonia synthesis is that nitrogen can

directly react with water, instead of an indirect route via H<sub>2</sub> and N<sub>2</sub>. However, electrochemical ammonia synthesis remains an unsolved research problem [10–13]. The reported electrochemical ammonia synthesis rates are below 10<sup>-9</sup> mol-NH<sub>3</sub> s<sup>-1</sup> cm<sup>-2</sup> at less than 20% FE (Faradaic efficiency) [9], while the required performance amounts to 10<sup>-6</sup> mol-NH<sub>3</sub> s<sup>-1</sup> cm<sup>-2</sup> with at least 50% FE [3,99]. False positives for electrochemical NH<sub>3</sub> synthesis have been reported in various studies, due to NH<sub>3</sub> or NO<sub>x</sub> contamination on the catalyst material, in the water, or in the N<sub>2</sub> gas [10,12,13,100–102]. Unless these scientific challenges are overcome, electrochemical ammonia synthesis cannot be considered as a feasible alternative for green ammonia production. Even so, various authors have



**Fig. 8 – Cost of the high-pressure electrolysis-based Haber-Bosch process with condensation (option a), and the low temperature, low pressure electrolysis-based single pass ammonia synthesis process as a function of the production capacity (option c). It is assumed that the installation is 350 days per year in operation at an electricity cost of 20 € MWh<sup>-1</sup> in 2030. The low cost estimates for the CapEx in Table S6 and Table S8 are used, which are the estimates with low temperature catalysts rather than with conventional Fe catalysts. It should be noted that Fig. 8 is the same as Figure S9 in the supplementary information. A sensitivity analysis for the CapEx and the energy consumption of the single pass process can be found in Figure S10 and Figure S11.**

performed techno-economic evaluations for a theoretical high performance catalyst for electrochemical ammonia synthesis [103–105]. From this it follows that the cost of ammonia from electrochemical ammonia synthesis is similar to that of the electrolysis-based Haber-Bosch process, only if the energy consumption is similar to that of the electrolysis-based Haber-Bosch process.

Photocatalytic ammonia synthesis has also gained attention in recent years [106,107]. The potential benefit for electrochemical ammonia synthesis, e.g. that nitrogen can directly react with water, also applies to photocatalytic ammonia synthesis. However, photocatalytic ammonia synthesis is even more complicated than electrochemical ammonia synthesis. Light is converted into electrons with a photo catalyst, which in turn should electrochemically convert N<sub>2</sub> and H<sub>2</sub>O into ammonia. Unsurprisingly, photocatalytic ammonia synthesis is still in the fundamental research phase [108,109].

Plasma-driven ammonia synthesis is also studied via NH<sub>3</sub> formation from N<sub>2</sub> and H<sub>2</sub>O, via NH<sub>3</sub> formation from N<sub>2</sub> and H<sub>2</sub>, and via plasma-based NO<sub>x</sub> synthesis with subsequent reduction to NH<sub>3</sub> [110–114]. A plasma is an ionized gas, in which highly energetic electrons may activate strong chemical bonds in gas molecules, such as N<sub>2</sub> [115,116]. This allows for weakening the N≡N bond. When coupled with catalysis, this potentially allows for N<sub>2</sub> activation at mild temperatures [117,118]. In practice, however, too much of the energy is lost as heat, which means plasma-based NH<sub>3</sub> processes cannot compete with the electrolysis-based Haber-Bosch process [119,120]. Plasma-based ammonia synthesis does not provide a cost advantage over the electrolysis-based Haber-Bosch process, even in the best-case scenario when the plasma would be able to supply

70 kJ mol<sup>-1</sup> enhancing N<sub>2</sub> dissociation without any additional heat losses [119].

Other technologies for ammonia synthesis include homogeneous catalysis [121,122], enzymatic reactions [123], and chemical looping [124]. However, these also have not found practical applications. In case of ammonia synthesis with homogeneous catalysis and enzymatic reactions, catalyst robustness is limited, and catalyst separation from the product is difficult. Chemical looping approaches suffer from complex non-steady state operation with large temperature and/or pressure fluctuations. Lastly, these technologies all have higher energy consumptions than the benchmark electrolysis-based Haber-Bosch process [56]. In conclusion, various novel methods for ammonia synthesis are researched. However, none of these technologies have proven to be feasible so far, implying that improving the thermo-catalytic process may be important in the upcoming decade(s).

## Outlook

The chemical industry of the 20th century and the first decades of the 21st century has been characterized by large-scale operation to minimize the contribution of the capital expenditure due to the economy of scale. This is possible because of availability of huge amounts of localized fossil resources that are easily transported to large-scale facilities. The net energy consumption for the best fossil-based ammonia synthesis plants nowadays is about 28 GJ t-NH<sub>3</sub><sup>-1</sup> [56]. However, an extensive network of heat exchangers is required to accomplish this due to large temperature changes within the ammonia synthesis process starting from methane, including steam-reforming. Thus, ammonia synthesis is currently only

economical feasible at large scale operation of 1000–6000 t-NH<sub>3</sub> d<sup>-1</sup> with an energy input of 0.4–2.5 GW [125]. Large-scale electrolysis-based ammonia synthesis plants consume about 30–35 GJ t-NH<sub>3</sub><sup>-1</sup> [18,91]. A benefit of electrolysis is that less heat integration is required as compared to steam methane reforming. However, the high-pressure Haber-Bosch synthesis loop still requires compression up to 100–300 bar, which is only economic for large-scale production.

With the availability of local, low-cost renewable electricity from solar and wind at the MW level, scale-down of such processes is desirable. Unfortunately, the relatively large CapEx (per ton product) at such scales often favors importing chemicals from large-scale plants over local production.

However, the development of low temperature ammonia synthesis catalysts and ammonia sorbents may allow for a shift in the paradigm. A single-pass process is conceivable due to higher achievable conversion to ammonia at low temperature and therefore low pressure (below 200 °C and at 15 bar). This lowers the ammonia synthesis cost by up to 60 € t-NH<sub>3</sub><sup>-1</sup> for small-scale operation of a few MW as compared to the conventional condensation-based synthesis loop. This is primarily due to a lower capital expenditure for the ammonia synthesis section, and more specifically a lower capital expenditure for heat exchange and compression. This allows for more effective scale-down of ammonia production at low temperature and pressure with intermittent renewable electricity for isolated communities in for instance the interior of Africa [18,21]. Transport of ammonia from centralized plants to isolated communities is typically too expensive [126]. Thus, the low temperature, low pressure, absorption enhanced, single pass ammonia synthesis process offers a near-term alternative for the high-pressure, condensation-based ammonia synthesis loop.

For such a single-pass ammonia synthesis process to be feasible, adequate absorbents and stable, low temperature ammonia synthesis catalysts must be developed. The mechanism of ammonia absorption-desorption in metal halides are well studied [61] and current research efforts should focus on the structure and morphology of supported, high-surface area absorbents in order to optimize the cyclic sorbent capacity, kinetics of absorption and desorption as well as durability. With the re-emergence of the field of thermo-catalytic ammonia synthesis, it is possible that very active catalysts operating at low temperatures will be developed in the upcoming years, given the rapid developments in the past few years with ammonia synthesis activity at temperatures down to 50 °C [29]. The long-term thermal stability as well as resistance against poisons such as H<sub>2</sub>O and O<sub>2</sub> of the second-generation Ru-based catalysts needs improvement before industrial operation becomes feasible. So far, a stable activity for only a few days has been reported [30]. Alternatively, non-noble catalysts with low-temperature activity may also be developed [84], resulting in lower material cost as compared to Ru-based catalysts.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2021.04.014>.

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